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Adsorption kinetics for the removal of copper(II) from aqueous solution by adsorbent PSTM-3T

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Abstract: The batch removal of copper (II) from aqueous solution under different experimental conditions using silicon-organic sorbent poly[N,N'-bis(3-silseskquioxanilpropyl)thiocarbamide] (PSTM-3T) was investigated in this study. This sorbent was produced from the hydrolytic poly-condensation reaction. The removal was favoured at pH = 5 for PSTM-3T. The effects of concentration and temperature have been reported. PSTM-3T was found to efficiently remove Cu(II) from solution. The batch sorption kinetics have been tested for a first-order reaction. The rate constants of adsorption have been calculated. The thermodynamic parameters (ΔG^0, K_c) obtained to indicate the endothermic nature of Cu(II) adsorption on PSTM-3T.

Keywords: Poly[N,N'-bis(3-silseskquioxanil)thiocarbamide], Langmuir, Freundlich isotherm, Thermodynamic parameters

Introduction

Adsorption processes for water treatment have had a long and productive history. Activated carbon has been widely used in wastewater treatment to remove organic and inorganic pollutants. It was also found that activated carbon has a great potential to remove heavy metals such as cadmium, chromium, lead and copper according to the reference [1].

Heavy metals are widely used in modern industries, including textile, leather, tanning, electroplating and metal finishing. They are released to environment either in treated wastewater to surface waters or as sludge applied to landfill. Copper is known to be a toxic metal. Because of its toxicity, it is imperative to significantly reduce its discharge levels [2].

The pre-concentration and separation of elements by use of chelating silicon organic [3-6] polymers have been reported. However, most of chelating silicon organic polymers are used for pre-concentration and determination of noble metal ions, the synthesis of silicon organic polymers usually takes a long time and the synthetic process is complicated.

Previously, we studied the removal of Cr(VI) from wastewater, using PSTM-3T and activated carbon produced from sawdust under selected conditions [7]. These were preliminary studies. In this research, we investigate the adsorption kinetics of PSTM-3T under wide range of conditions.

Experimental

Materials characterization

Silicon-organic polymer $[-O_{1.5}Si(CH_2)_3HNC(S)NH(CH_2)_3SiO_{1.5}-]_n$ – poly[N,N'-bis(3-silseskquioxanilpropyl)thiocarbamide] used in this study was synthesized [3] in Russia.

The adsorbent used in this work were characterized by scanning electron microscope (SEM) (Fig. 1). This figure shows that the PSTM-3T has an irregular and porous surface, which indicates high surface areas. Moreover, the surface area of PSTM-3T is 490 m^2/g and the total pore volume is 3.53 ml/g.

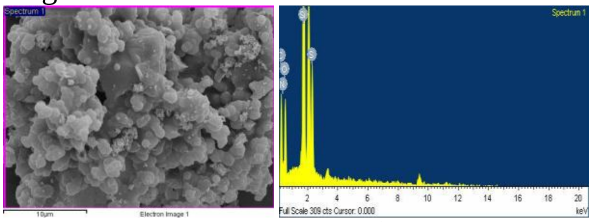

Fig. 1. SEM/EDS image of PSTM-3T

Energy dispersive spectrometer (EDS) was also used to analyze sorbent PSTM-3T. The EDS analyses provided a rudimentary and after adsorbed copper compositions for the PSTM-3T. The compositions from the peak areas (Fig.1) are calculated as shown in Table 1.

Table 1. EDS composition of PSTM-3T

Element	Weight (%)	Atomic, (%)
Silica (Si)	18.40	10.20
Carbon (C)	36.94	47.90
Oxygen (O)	23.16	22.54
Sulfur (S)	7.27	3.53
Nitrogen(N)	14.23	15.83

Adsorption

The measurement of adsorption kinetics of the PSTM-3T was carried out by shaking 0.05 g of PSTM-3T with 50 ml of Cu(II) solution of known concentration in 100 ml conical flask placed in a stirrer/hot plate (Corning PC-620D) provided with a temperature controller. The removal kinetics of the Cu(II) was investigated by drawing samples after the desired contact time and the filtrate was analyzed for the remaining Cu(II) concentration. A spectrophotometer (HITACHI, U-1000) was employed at a wavelength of 430 nm with sodium diethyl dithiocarbamate reagent to determine the remaining concentrations of Cu(II) in each sample solutions after adsorption at the desired time intervals. The analysis was carried out according to the procedure given by the reference [8]. The same procedure has been used to study the effect of initial concentration, pH and temperature. The pH was adjusted with either 0.1 M HCI or 0.1 M NaOH as required.

The equilibrium isotherm was determined by mixing 0.05 g of PSTM-3T with 50 ml of copper solution in 100 ml conical flask at the required temperature. Each isotherm consisted of nine copper concentrations varied from 1000 to 10000 ppm. The flasks containing copper solution and PSTM-3T were placed in a shaker and agitated for 40 min at the required temperature and at a fixed agitation speed of 500 rpm. The equilibrium concentrations were measured by the spectrophotometer and referenced with the calibration curve. The equilibrium adsorption capacity was calculated using the equation: $q_e = (C_0 - C)V/M$ (1) where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C are the initial and equilibrium concentration (mg/l) of Cu(II) ions in solution, V(l) is the volume and M (g) is the weight of sorbent.

The accuracy of temperature and concentration measurements was ± 0.5^0C and ± 0.02 ppm, respectively.

Results and Discussions

Effect of pH

The adsorption of Cu(II) by PSTM-3T at different pHs at an initial concentration of 20 mg/l and a temperature of 90^0C is shown in Fig. 2. For PSTM-3T, particle size was 0.2 mm. For PSTM-3T, the amount adsorbed increases from 2.0 to 7.0 mg/g as the pH decreases from 5 to 2. This indicates that the adsorption capacity of the adsorbent is clearly pH dependent. It is obvious that pH determines the extent of the Cu(II) removal as well as providing a favourable adsorbent surface charge for the adsorption to occur.

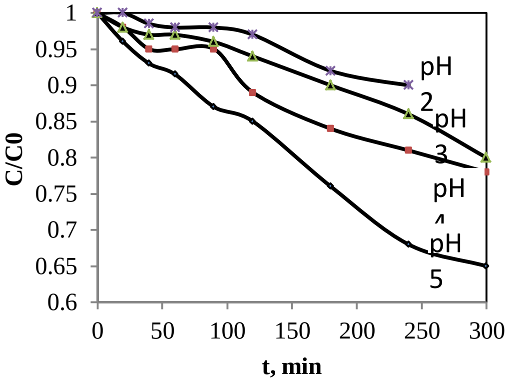

Fig.2. Time variation of Cu(II) adsorption on PSTM-3T at different pHs.

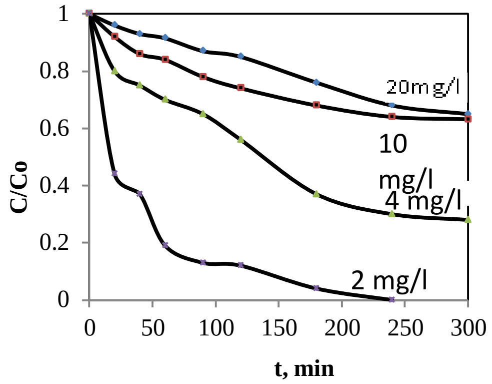

Fig.3. Time variation of Cu(II) adsorption on PSTM-3T at different initial concentrations.

Cu(II) exists in different forms in aqueous solution and the stability of these forms is dependent on the pH of the system. A characteristic of the sorption of heavy metal ions onto the surface is that at a set bulk solution heavy metal concentration the sorption is greatest at a pH value that is just slightly more acidic than the pH at which there is bulk precipitation of the metal hydroxide. As pH is further raised, once the bulk solubility limit is reached, the sorption is greatly reduced because the metal ion is removed from solution by the bulk precipitation. The relative concentration of Cu(II) species in system containing 1× 10^{-4} mol/l Cu(II) [2] is shown in Fig.4. This figure clearly shows Cu(II) species distribution for a total Cu(II) concentration of 1× 10^{-4} mol/l. It is noted that maximum sorption of Cu(II) occurs at a pH value slightly more acidic than the pH of bulk precipitation of $Cu(OH)_2$.

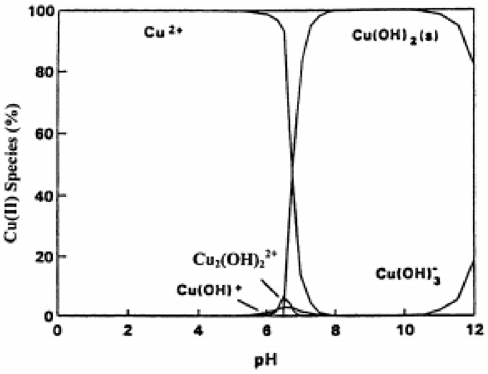

Fig. 4. Relative concentration of Cu (II) species in a system containing 1*10^{-4} mol/l Cu(II); from Schneider (1995).

The Cu(II) form is also stable within the low pH range, however, its concentration decreases sharply in aqueous solution with increasing pH. Maximum adsorption at pH=5 indicates that it is the Cu(II). Form of Cu(II), which is the predominant species between pH=1 and 5, which is adsorbed preferentially on the PSTM-3T.

3.2. Effect of initial concentration

The removal of Cu(II) adsorption on PSTM-3T is shown in Fig. 3 to increase with time and attains a maximum value at about 180 min, and thereafter, it remains almost constant. On changing the initial concentration of Cu(II) solution from 2 to 20mg/l, the amount adsorbed increases from 2.0 to 7.0 mg/g at pH=5 using PSTM-3T with average particle size of 0.2 mm (Fig. 3). From Fig.3, it can be seen that the amount of adsorbate with low initial concentration attained on the solid phase is smaller than the amount attained when high initial concentrations are used. However, the percentage removal of Cu(II) for the PSTM-3T is not similar with lower initial concentrations and higher initial concentrations.

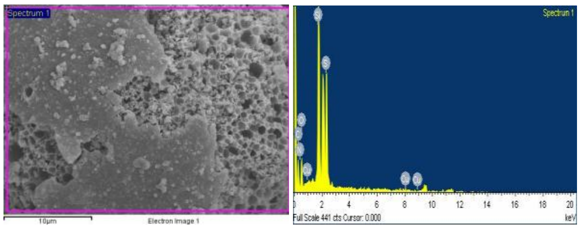

Fig.5. SEM/EDS images of PSTM-3T after adsorbed Cu(II)

The PSTM-3T after adsorbed of Cu(II) was characterized by scanning electron microscope (SEM) and the EDS analysis (Fig. 5). The compositions from the peak areas are calculated as shown in Table 2.

Table 2. EDS composition of PSTM-3T after adsorbed Cu(II)

Elements	Weight, %	Atomic, %
Carbon (C)	42.81	58.68
Silica (Si)	20.68	12.12
Oxygen (O)	18.45	18.99
Sulfur (S)	16.35	8.40
Nitrogen (N)	1.49	1.76
Copper (Cu)	0.21	0.05

Effect of temperature

The adsorption of Cu(II) on the PSTM-3T at different temperatures increases in the adsorption capacity when the temperature is increased. The adsorption capacity varies with temperature and initial concentration as shown in Fig.6. With increase in temperature from 298 to 363K, the adsorption capacity increased from 4.80 to 8.60 mg/g for the initial concentration of 10 mg/l at pH 5.0. Similar trends are observed for all the other concentrations. This indicates that the adsorption reaction is endothermic in nature.

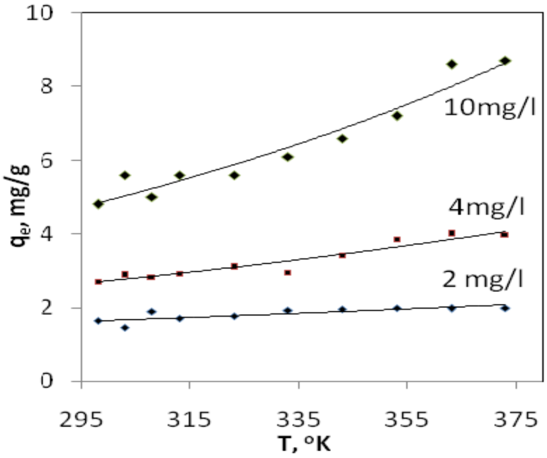

Fig.6. Effect of temperature for the different concentrations at pH = 5.0.

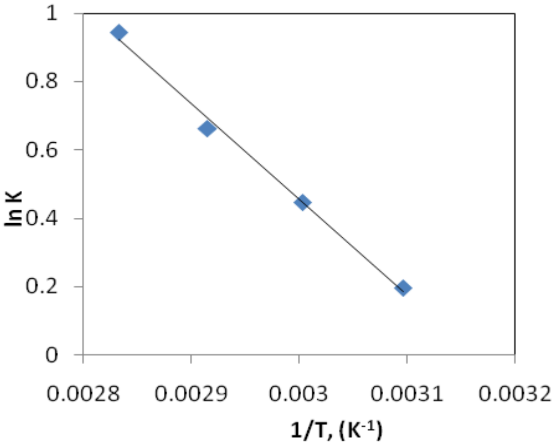

Fig.7. Vant Hoff's plot at concentration of 10 mg/l, pH 5.0.

The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intra-particle diffusion of Cu(II) ions into the pores of the sorbent at higher temperatures[9]. The standard Gibb's energy was evaluated by

$$\Delta G^0 = - RT \ln K_c \qquad (2)$$

The equilibrium constants K_c was calculated at each temperature using the following relationship

$$K_c = C_{Ae} / C_e \qquad (3)$$

where C_{Ae} is the amount adsorbed on solid at equilibrium and C_e is the equilibrium concentration.

The other thermodynamic parameters such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined using the following equations

$$\text{Ln } K_c = \Delta S^0 / R - \Delta H^0 / RT \qquad (4)$$

ΔH^0 and ΔS^0 were obtained from the slope and intercept of the Vant Hoff's plot of ln K_c versus 1/ T as shown in Fig.7. Positive value of ΔH^0 indicates that the adsorption process is endothermic. The negative values of ΔG^0 reflect the feasibility of the process and the values become more negative with increase in temperature. Standard entropy determines the disorderliness of the adsorption at solid-liquid interface. Table 3 summarizes the results.

Table 3. Thermodynamic parameters of PSTM-3T at initial concentration of 10 mg / l, pH5.0

T (K)	ΔG (kJ/ mol)	ΔH (kJ / mol)	ΔS (J / mol k)
323	-0.526		
333	-1.237	28.33	11.64
343	-1.890		
343	-2.770		

Adsorption kinetics modeling

The models of adsorption kinetics correlate the solute adsorption rate, thus these models are important in water treatment process design. In this study, the adsorption dynamics were followed by conducting the adsorption of Cu(II) on the adsorbent for a batch reaction as described before.

Pseudo-first-order model

The sorption kinetics may also be described by a pseudo-first-order according to Ho and McKay [1] and Namasivayam and Kardivelu [10]:

$$dq/dt = k'(q_e - q) \qquad (5)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q the amount of solute adsorbed at any time (mg/g) and k' is the adsorption constant. Equation (5) is integrated for the boundary conditions t = 0 to >0 (q = 0 to >0) and then rearranged to obtain the following linear time dependence function:

$$\log(q_e - q) = \log(q_e) - k't/2.303 \quad (6)$$

Plot for equation (6) was made for PSTM-3T at different pHs, different initial concentrations. Fig.8 is shown as an example for these plots. Approximately, linear fits are observed for all pHs, concentrations indicating that sorption reaction can be approximated to first-order kinetics. The smallest correlation coefficient in case of pH=2 was 0.863, which is even better than the second-order reaction model (Figure not shown). The highest correlation coefficient was 0.995 for pH=4 (Table 3).

The highest removal efficiency of PSTM-3T for 2 mg/l and 4 mg/l of Cu(II) was found 99.9% and 99.5% respectability (Table 4). The increase in the efficiency of removal may be attributed to the fact that with an increase in the adsorbent dosage, more adsorbent surface is available for the solute to be adsorbed [11].

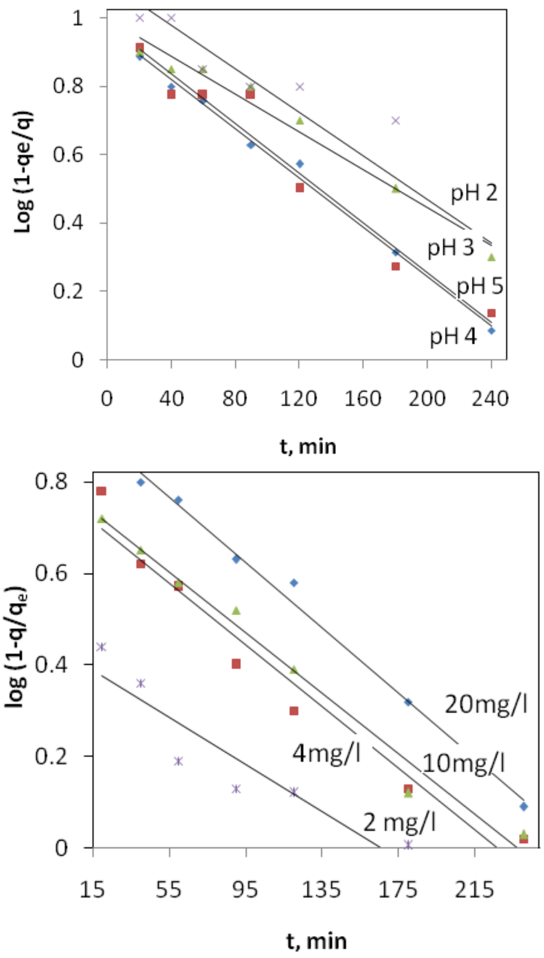

Fig.8. First-order kinetics plot for adsorption of Cu(II) on PSTM-3T at different pHs and at different initial concentrations.

Constant k' for all situations tested have been calculated and summarized in Tables 3, 4.

Table 4. The first-order reaction rate constants for PSTM-3T at different pHs[a]

Sorbent	pH	k'(min^{-1})	r^2	R (%)
PSTM-3T	2	0.0050	0.863	10.0
	3	0.0024	0.971	20.0
	4	0.0030	0.995	22.0
	5	0.0034	0.953	35.0

[a] Temperature = 90^{0}C, particle size = 0.2 mm, initial concentration = 20 mgl.

Table 5. The first-order reaction rate constants for PSTM-3T at differentinitial concentrations[a]

Sorbent	C$_0$ (mg/l)	k' (min^{-1})	r^2	R (%)
PSTM-3T	2	0.0076	0.862	99.9
	4	0.0036	0.957	99.5
	10	0.0028	0.982	87.0
	20	0.0032	0.993	35.0

[a] Temperature = 90^{0}C, particle size = 0.2 mm, pH = 5

Adsorption isotherm

The equilibrium data for adsorption of Cu(II) on to the PSTM-3T may follow the rearranged Langmuir equation [11]:

$$C_e / q_e = 1/ Q^0 b + C_e / Q^0 \qquad (7)$$

Where C_e is the equilibrium concentration (mg / l) and q_e the amount adsorbed at equilibrium (mg / g). The Langmuir constants Q^0 and b, which are related to the adsorption capacity and heat of adsorption, respectively, were determined (Table 5) from the slope and intercepts of the linear plots of C_e / q_e versus C_e ().

Table 6. Langmuir and Freundlich constants for PSTM-3T at 298 K

Sorbent		Langmuir		Freundlich	
	T (K)	Q^0 (mg/g)	b	K_f (mg/g)	n
PSTM-3T	298	16.0	12.19	1.66	0.13

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as [11] $\ln q_e = \ln K_f + b_f \ln C_e$ (8)

where K_f indicates adsorption capacity (mg / g) and b_f an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the sorbent. For values in the range $0.1 < b_f < 1$, adsorption is favorable [11].

Conclusion

Synthesized poly[N,N'-bis(3-silseskquioxanilpropyl)thiocarbamide] is used for the removal of Cu(II) from aqueous solution. Sorption of Cu(II) is found to be effective in the low pH range and at higher temperatures. Increase in adsorption with rise in temperature reveals that the adsorption is chemical in nature and the process is endothermic, which is confirmed by the thermodynamic parameters evaluated. The Langmuir isotherm fits the data better than the Freundlich isotherm. Thus, the results shows that the PSTM-3T can be effectively applied for the removal of Cu(II) from natural water where is the content of Cu(II) lower than 10 mg/l.

References

1. G. McKay, M.J. Bino, A.R. Altamemi, The adsorption of various pollutants from aqueous solutions onto activated carbon, Water Res. 19 (4), (1985) pp.491-495.
2. Ivo A.H. Schneider, Jorge Rubio, Ross W. Smith, Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation, Int. J. Mineral Processing 62 (2001) pp.111-120.
3. Boronkov M. G., Vlasova N. N., Pozidaev Yu. N., Pestunovich A. E., Kirillov A. I., Visokoeffectivnii kompleksit I amfolit – poly[N,N'-bis(3-silseskquioxanilpropyl)thiocarbamide] , DAN SSSR, T.320, № 3 (1991) p.658-662.
4. Burmaa Gunchin, Sorbtsionnie svoistva kremniiorganicheskikh polymerov s carbofunktsionalnimi thiouriednimi gruppami po otnosheniyu k zolotu i serebru, Avtoref. (1992) 18p.
5. Burmaa G., Organosilicon polymers as an effective sorbents for gold(III), Reports of the Chemistry Institute, MAS, (1995) p.1-5.
6. G. Burmaa, I. Sukhbaatar, Yu. Ganchimeg, Sorption activities and mechanism of silicon organic polymers for Noble metals (Au, Ag, Pt, Pd, Rh), MUST, MTS, Erdem shinjilgeenii byteeliin emkhetgel, № 2/114, (2010) pp.215-221.
7. T. Azzaya, G. Burmaa, R. Egashira, Sh. Nyamdelger Comparison of the adsorption activity of chromium from tannery wastewater by Pinus activated carbon and silicon organic polymer PSTM-3T
8. Unifitsirobannie metodi analisa vod, Pod obshei redaktsiei Yu. Yu. Lurie, (1973) p. 270-273.
9. J. Chen, S. Yiacoumi, T. G. Blaydes, Equilibrium and kinetic study of copper adsorption by activated carbon, Sep. Technol. 6 (1996) p.133-146.

10. C. Namasivayam, K. Kardivelu, Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product, Carbon 37 (1999) p.79-84.
11. Salim, M. and Munekage, Y. Removal of Arsenic from aqueous solution using silica ceramic: Adsorption kinetic and equilibrium studies, Int. J. of Environm. Res. Vol. 3, No 1, (2009) p.13-22.